Rapid Determination of Sorption Affinity of Phosphine by Fumigation within a Gas Chromatographic Column

B. Berck[1] and F. A. Gunther[2]

A rapid, dynamic method of measuring sorption affinity of granular or powdered substrates toward phosphine, PH_3, in the ppb–ppt range was developed. The method employs rapid fumigation (0.5 to 6 seconds contact time) within a GC column. A small amount of substrate (0.15 to 2 grams) is packed in a short Teflon or glass column ($^1/_4$-in. o.d. and 1 to 6 in. long) attached to an 18-inch empty Teflon or stainless steel column; 500 picograms of PH_3 are injected into the N_2 carrier gas stream. The response (peak height) measured by flame photometric detection (Berck et al., J. AGR. FOOD CHEM., 1970) is compared with that obtained with an empty column. Uptake by the substrate can be measured to 5 picograms (1% level) with a detector response within 15 seconds after injection of 500 picograms of PH_3. When column temperatures are raised, chemisorption is indicated if the response is significantly lowered, and physisorption if the response is thereby increased. The substrates included ground wheat, wheat flours, rye flour, soy flour, middlings, shorts, bran, semolina, wheat germ, starch, gluten powder, fish protein concentrate, casein hydrolysate, glutathione (oxidized and reduced forms), aluminum oxide, three types of soil, and glass beads. The method can be adapted to investigate sorption affinity of other gases applied to virtually any granular or powdered substrate that would be stable under the test conditions.

Sorption is a blanket term first introduced by McBain (1926) to include both chemisorption (adsorption with chemical reaction or conversion at surfaces) and physisorption (physical adsorption and absorption), respectively. Sorption of solids, liquids, and gases is involved in many thousands of diverse organic and inorganic systems. The 13,763 references for the period 1943–53 compiled by Deitz (1956) as an annotated bibliography on solid adsorbents are an indication of the large volume of scientific activity directed to the investigation of sorption. We estimate an additional 20,000 investigations thereon since 1953. The differentiation of chemisorption (nonrecoverable, chemically bound, irreversible) from physisorption (reversible; desorbed by increase of temperature, reduction of atmospheric pressure, extraction with solvents, or prolonged aeration with inert gases) is treated in texts by Garner (1957), Gregg and Sing (1967), Hayward and Trapnell (1964), and Young and Crowell (1962), among others.

Sorption influences distribution-persistence (concentration-time) relationships, bioactivity, and interactions of fumigants with many kinds of substrates, and is known to be affected by particle size, moisture content, and nature of substrate, as well as by fumigant dosage, temperature, and contact time. Such aspects are reviewed by Lindgren and Vincent (1962) and by Berck (1964; 1965a). Differential sorption behavior of wheat and other cereal products as chromatographic columns toward fumigant gases was shown by Berck (1956; 1961; 1965b; 1968b) and by Berck and Solomon (1962). Static and semidynamic methods of fumigant application, with exposure periods ranging from 5 hours to 13 days, were used in the foregoing investigations.

Berck (1968b) obtained presumptive evidence of chemisorption of phosphine, PH_3, by exposing cereal products in closed systems for periods up to 7 days and then aerating with N_2 at 180 cc./minute for 30 minutes. As the adequacy of this aeration period was questioned (Rauscher and Mayr, 1968), the present study was undertaken, as described below. The main feature distinguishing the current work from all previous investigations is the use of short exposure periods combined with continuous, uninterrupted aeration of the substrates with N_2 as a sweep gas.

This report deals with a dynamic method of measuring the sorption affinity of granular or powdered substrates toward fumigant gases by "flash fumigation" within a GC column, whereby the column packing is also the sample. A small amount of substrate (0.15–2 g.) is vibration-packed to a $^3/_4$- to 6-inch length in a short Teflon or glass column ($^1/_4$ inch o.d. and $6^1/_2$ inches long) attached to an 18-inch empty Teflon or stainless-steel column. After an aeration (degassing) with N_2 carrier gas of 2 minutes, 500 picograms of PH_3 are injected into the gas stream. The response (peak height) measured by flame photometric detection (FPD) (Berck et al., 1970) is compared with that obtained with an empty column. Sorption effects can be quantitatively assessed to within 1% (5 pg.) of the amount applied. When column temperatures are raised, chemisorption is indicated if the response is significantly lowered, and physisorption if the response remains static or is increased thereby. Depending on the column temperature and the nature and length of the column packing, the net PH_3 residence or exposure time ranged from 0.5 to 6 seconds (cf. 5 to 24 hours in conventional fumigant research methods). The FPD response was obtained generally within 15 seconds after injection of a 500-picogram pulse of PH_3. The method can be adapted to investigate sorption affinity of other gases applied to virtually any granular or powdered substrate that would be stable under the test conditions. Thus, the uptake of methyl bromide by cereal products, soils, and miscellaneous substrates was determined similarly in a gas chromatograph equipped with a hydrogen flame ionization detector (Berck and Kolbezen, 1970).

EXPERIMENTAL

Materials and Apparatus. GAS CHROMATOGRAPHIC EQUIPMENT. The gas chromatographic equipment and operational parameters used for flame photometric detection of PH_3 have been described (Berck et al., 1970). Column temperatures varied from 45° to 130° C. for particular experimental requirements.

[1] Canada Department of Agriculture, Research Station, Winnipeg 19, Manitoba
[2] Department of Entomology, University of California, Riverside, Calif. 92502

Table I. Percentage of Applied PH₃ Sorbed by Substrates Used as Column Packings[a]

Column Specifications	Column Temperature, ° C.							
	50	60	70	80	90	100	110	120
1. Wheat, coarse ground, 20–40 mesh, 9.0% moisture, 6-inch, 2.08 g.	20.0	17.0	16.0	18.1	17.6	15.5	17.5	
2. Wheat, coarse ground, 20–40 mesh, 11.0% moisture, 6-inch, 2.2 g.	30.0	27.0	25.0	26.0	22.8	20.5	20.4	
3. Wheat, coarse ground, 20–40 mesh, 15.0% moisture, 6-inch, 1.95 g.	31.5	42.5	47.0	48.5	50.0	50.0		
4. Wheat, coarse ground, 20–40 mesh, 17.5% moisture, 6-inch, 1.81 g.	60.0	58.5	57.3	58.2	58.5	59.4		
5. Wheat flour, 1st patent, 13.9% moisture, 3-inch, 1.00 g.	11.0	10.2	10.5	9.0	7.0	9.0		
6. Wheat flour, 2nd patent, 14.0% moisture, 3-inch, 1.04 g.	34.5	52.0	53.0	52.2	50.8	48.5		
7. Rye flour, 13.1% moisture, 3-inch, 0.9 g.	61.8	60.5	56.3	49.2	40.0			
8. Middlings, 13.5% moisture, 3-inch, 0.95 g.	9.5	14.0	18.0	25.5	33.0			
9. Shorts, 13.8% moisture, 3-inch, 0.80 g.	16.0		17.0		28.0			
10. Bran, 14.0% moisture, 6-inch, 0.6 g.	32.8	35.0	38.0	42.0	42.2	43.5	44.2	47.5
11. Semolina, 14.1% moisture, 6-inch, 1.95 g.	9.5	12.5	16.0	18.5	24.5	28.5		
12. Wheat germ, 13.0% moisture, raw, 6-inch, 1.28 g.	4.5	1.0	4.0	6.5	9.5	16.0		
13. Wheat starch, 9.1% moisture, 3-inch, 0.95 g.	19.5	15.5	13.5	11.0	10.5	9.6		
14. Wheat gluten powder, 5.5% moisture, 3-inch, 0.86 g.	85.2	87.6	89.7	96.0	100.0			
15. Soy flour, 5.7% moisture, 3-inch, 0.77 g.	97.0	100.0						
16. Fish protein concentrate powder, 7.0% moisture, 0.38 g.	25.0	37.5	41.5	49.2	53.0	64.0	69.4	
17. Casein hydrolysate powder, 5.1% moisture, 1½-inch, 0.36 g.	44.0	57.5	78.8	88.1	94.6	100.0		
18. Aluminum oxide, Al₂O₃, Merck, chromatographic grade, 1½ inch, 0.88 g.	22.0		20.4		16.0		16.5	16.0
19. Peat soil, 2-inch, 0.75 g.	50.0	48.0	50.0	49.2	50.0	50.7	50.8	56.1
20. Yolo soil (montmorillonite), 1½-inch, 0.99 g.	33.5		38.0		57.5		82.7	
21. Ramona soil (mica), 1½-inch, 1.07 g.	54.0		56.0		78.0	93.4	98.0	

[a] Each packed column (1-, 1½-, 3-, or 6-inch Teflon, ¼-inch o.d.) was coupled to an 18-inch empty Teflon column. The mean peak heights of the packed columns resulting from triplicate injections of 500 pg. of PH₃ into the N₂ carrier gas stream are expressed as % sorption (the fraction not recovered) in comparison to the responses of the unpacked column at the various temperatures shown. The data are uncorrected for variable increase in retention time shown by the packed columns (0.5–6 seconds more than the empty column, depending on the column specifications and column temperature). This footnote also applies to Table II.

Gas concentrate flasks, phosphine standards, and syringes have been described (Berck et al., 1970).

COLUMNS. Two empty Teflon columns, ¼-inch o.d. and 24 inches and 18 inches long, respectively, and for cross reference, two empty stainless steel (s.s.) columns, ¼-inch o.d. and 24 inches and 18 inches long, were used. Short Teflon columns, 6¾ inches long, were coupled to the 18-inch empty columns with Teflon ferrules and hexagon nuts at the coupled ends, and with Swagelok ferrules and s.s. hexagon nuts at the inlet and exit ends of each coupled column. The short columns were vibration-packed with the substrate to yield packed columns of 1, 1½, 3, or 6 inches, using about ³/₈ inch of glass wool at each end to contain the column packing.

For data of Table III, two types of borosilicate glass columns were used: small glass columns, 3 inches × 6.5 mm. o.d. (approx. 4.0 mm. i.d.) were vibration-packed with cereal substrates to contain a net column length of 2 inches. The large glass columns consisted of 2 inches of 13 mm. o.d. glass tubing butt-sealed at both ends to 6.5 mm. o.d. tubing. The length of the zone packed in each large column was approximately the same as that of the small columns, but the total weight of packing was 4 to 5 times greater.

SUBSTRATES. The cereal products and other substrates used in this investigation are listed in Tables I, II, and III. Cleaned Canadian wheat, Hard Red Spring, 2 Northern grade, was used. Moisture levels above 9.0% were obtained by adding calculated amounts of water to the wheat seeds (tempering) and allowing to equilibrate in closed containers for 48 hours at room temperature. The seeds were coarsely ground in 50-g. amounts in a small mechanical coffee grinder equipped with

Table II. Comparative % Sorption of PH₃ by Additional Materials Used as Column Packings

Column Specifications	Column Temperature, ° C.			
	45	70	95	120
1. Glass beads, "Glasperlen" (B. Braun, Melsungen, Germany) 1.0–1.05 mm. diam., 1½ inch, 1.29 g.	15.0	13.8	14.2	14.0
2. Peat soil,[a] Stockton, Calif., 1½ inch, 0.58 g.	30.0	30.5	35.0	41.6
3. Yolo soil[a] (montmorillonite), 1½ inch, 1.0 g.	61.8	71.9	75.1	86.2
4. Ramona soil[a] (mica), Riverside, Calif., 1½ inch, 1.5 g.	72.7	81.3	89.4	94.1
5. Zaca soil, 1½ inch, 0.95 g.	33.0	52.3	68.4	78.1
6. Glutathione oxidized (GSSG), 1½ inch, 0.15 g.	40.0	42.9	45.5	
7. Glutathione reduced (GSHG), 1½ inch, 0.20 g.	47.4	51.7	56.1	

[a] These samples are similar to those designated as column numbers 19–21 of Table I, but were checked 6 months later.

stainless steel blades, and were sieved to retain a 20–40 mesh size after grinding.

The wheat flours, rye flour, middlings, shorts, bran, semolina, raw wheat germ, wheat starch (<200 mesh), and wheat gluten powder (80–100 mesh) were conventional run-of-the-mill grades. The soy flour (Nutrisoy brand, Archer–Daniels–Midland Co., Minneapolis, Minn.) was a refined, low fat (1%) and low moisture (5.7%) soy product used as a protein supplement and milk replacement in animal feeding, with contents of

Table III. Deviations in % Sorption of PH_3 by Cereal Substrates Packed in Small vs. Large Capacity Glass Columns[a]

Column Packing	Small Column, g.	Column Temp. °C			Large Column, g.	Column Temp. °C		
		45	70	95		45	70	95
A. Wheat flour, first patent	0.56	11.8	10.8	10.5	2.37	20.0	19.3	20.5
	0.53	11.4	9.4	9.6	2.48	26.7	24.3	23.4
	0.54	14.1	12.5	10.5	2.58	20.7	19.8	19.5
	0.58	14.5	11.5	10.5	2.50	17.4	17.1	16.8
	0.52	9.3	8.8	7.6	2.48	23.4	20.4	20.1
	0.53	9.9	9.1	7.6	2.54	18.0	17.1	16.8
Mean % sorption		11.8	10.4	9.4		21.0	19.7	19.5
Std. deviation		2.13	1.48	1.42		3.50	2.66	2.50
Std. error		0.87	0.60	0.58		1.43	1.08	1.02
B. Wheat flour, second patent	0.48	30.0	28.7	29.4	2.41	39.6	41.9	42.8
	0.49	28.0	26.6	25.2	2.47	41.2	44.3	44.7
	0.47	22.2	21.6	21.0	2.44	40.6	43.0	44.2
	0.49	29.2	28.2	31.0	2.52	38.8	44.3	44.8
	0.48	29.2	27.6	28.8	2.40	39.5	39.0	38.0
	0.47	26.7	27.6	26.2	2.50	41.6	42.3	52.7
Mean % sorption		27.6	26.7	26.9		40.2	42.5	42.9
Std. deviation		2.86	2.60	3.60		1.09	1.97	2.55
Std. error		1.17	1.06	1.47		0.44	0.80	1.04
C. Feed middlings	0.46	47.3	47.0	52.5	2.30	60.6	61.6	70.2
	0.45	43.8	48.0	50.5	2.10	58.5	61.6	69.8
	0.53	51.8	51.8	60.5	2.16	52.0	56.2	66.6
	0.51	51.8	52.5	59.5	2.22	51.3	54.9	60.3
	0.52	49.0	53.8	59.2	2.15	57.8	59.3	63.9
	0.44	48.0	49.4	48.4	2.27	59.2	63.9	68.8
Mean % sorption		48.6	50.4	55.1		56.6	59.6	66.6
Std. deviation		3.02	2.69	5.26		3.93	3.47	3.87
Std. error		1.23	1.10	2.15		1.60	1.42	1.58
D. Wheat shorts	0.29	37.2	41.0	47.5	1.50	52.6	58.8	64.8
	0.27	35.5	42.8	51.5	1.39	53.5	59.0	63.8
	0.28	41.8	48.5	56.0	1.41	48.2	56.0	63.2
	0.28	43.0	51.7	57.6	1.38	46.5	52.5	62.2
	0.29	41.6	45.8	52.2	1.45	48.2	53.5	61.6
	0.26	36.2	41.1	45.5	1.42	46.8	52.1	59.4
Mean % sorption		39.2	45.2	51.7		49.3	55.3	62.5
Std. deviation		3.27	4.33	4.68		3.00	3.09	1.90
Std. error		1.34	1.77	1.91		1.22	1.26	0.77
E. Gluten powder	0.61	84.4	90.6	94.1	3.12	88.6	89.7	93.0
	0.61	76.4	84.9	91.9	2.78	87.3	88.9	93.0
	0.63	81.8	88.4	92.1	2.95	89.9	92.4	94.8
	0.66	80.9	89.6	95.3	3.18	92.5	93.6	95.8
	0.60	77.2	86.4	92.9	3.05	91.7	94.8	96.8
	0.64	79.7	84.8	93.1	3.02	90.5	95.4	97.2
Mean % sorption		80.1	87.4	93.2		90.1	92.5	95.1
Std. deviation		2.98	2.45	1.28		1.93	2.67	1.83
Std. error		1.21	1.00	0.52		0.79	1.09	0.75
F. Soy flour	0.54	86.3	96.3	100.0				
	0.57	89.1	99.9	100.0				
	0.51	95.1	99.2	100.0				
	0.59	93.9	98.5	100.0				
	0.56	94.6	99.6	100.0				
	0.53	94.2	100.0	100.0				
Mean % sorption		92.2	98.9	100.0				
Std. deviation		3.62	1.39	0.00				
Std. error		1.48	0.57	0.00				

[a] Small borosilicate glass columns, 75 mm. × 6.5 mm. o.d. (approx. 4.0 mm. i.d.) were vibration-packed with cereal substrates to contain a net column length of 2 inches. Their larger counterparts consisted of 2 inches of 13-mm. o.d. glass tubing butt-sealed at both ends to 6.5-mm. o.d. tubing. The length of packing of each large column was approximately the same as that of a small column, but the total weight of packing was 4 to 5 times greater. Six small and six large columns were evaluated for each substrate on the basis of the comparative responses (peak heights) obtained from triplicate injections of 500 pg. of PH_3 into packed vs. empty columns at 45°, 70°, and 95° C., respectively.

protein, sucrose, and total carbohydrate of 52, 8, and 34.5%, respectively. The fish protein concentrate (FPC) powder, (Viobin Corporation, Monticello, Ill.), had protein, ash, fat, and moisture contents of 74.6, 17.1, 1.4, and 7.0%, respectively. The casein hydrolysate, enzymatic (Merck and Co., Rahway, N. J.) provided mixed amino acids from an animal protein source of 95% protein content. Glutathione in both oxidized (GSSG) and reduced (GSHG) forms (Mann Re-

search Laboratories, New York, N. Y., 10006) was used to determine the effect of oxidative state on sorption affinity for PH_3. Peat (organic), Yolo (montmorillonite) and Ramona (mica) soils, (Dept. of Soils and Plant Nutrition, University of California, Riverside, Calif. 92502), represent three distinctive and well-characterized soil types. The glass beads were used to determine the possibility of PH_3 sorption by an ostensibly inert material. Powdered Al_2O_3, Merck, chromatographic

grade, and Woelm, chromatographic grade, were tested for sorption of PH_3 in both the presence and absence of S-containing gases (Berck et al., 1970).

General Procedure. The approximate weights of substrate needed for 1-, $1\frac{1}{2}$-, 3-, or 6-inch packed columns were determined and columns were vibration-packed and coupled to the empty column, as described above. After flushing for 2 minutes with N_2 at the column temperature selected, 500 picograms of PH_3 were injected in triplicate with a 10-μl. syringe. The FPD response to the PH_3 injection was compared with that obtained with the same amount in the empty column of the same overall length. Determinations were made in triplicate at each temperature. For most substrates, temperatures did not exceed 100° C. to avoid effects of partial decomposition, but for soils and products that showed no evidence of decomposition, as indicated by steady base lines and flame stability, temperatures as high as 120° C. were used. To disconnect a column in the gas chromatograph, the nut at the N_2 inlet side or at the column-coupling point is loosened sufficiently to vent the gas pressure before disconnecting the nut at the N_2 exit side. This prevents possible blow-out of the column packing, particularly with glass columns. In connecting the column assembly, the exit side is tightened first.

RESULTS AND DISCUSSION

Table I shows the comparative % sorption of PH_3 at temperatures ranging from 50° to 120° C. by various materials used as packings in short GC columns. Variable sorption is shown, with overtones of specificity that suggest chemisorption in some instances. The values for wheat (items 1 to 4) indicate that sorption of PH_3 is directly related to moisture content of the seeds, in agreement with previous findings (Berck, 1968b) employing potentiometric titration (Berck, 1968a). At higher temperatures, wheats of 9 and 11% moisture contents show a drop in % sorption, indicative of physisorption, whereas wheat of 15% moisture content shows an increase in % sorption, indicative of chemisorption. Wheat of 17.5% moisture content (item 4) has a higher sorption affinity than that shown by wheats 1 to 3, but the sorption trend varies little with temperature. Perhaps the steady state results from drying of the substrate at the higher column temperatures through removal of water vapor by the carrier gas (dry N_2). A similar trend is also shown by the 15% moisture content of wheat at the higher column temperatures.

Significant differences due to types of flour are shown by items 5, 6, and 7 (Table I). Thus, first patent flour (item 5) shows the least sorption, and little change in sorption in response to rising temperature. Rye flour (item 7) shows a higher uptake of PH_3 at 50° C., but sorption is lower at the higher temperatures, indicative of physisorption. The PH_3 uptake of second patent flour (item 6) is intermediate between first patent and rye flours, and shows a sharp rise (chemisorption) at 60° C., followed by a steady state. Greater uptake of PH_3 by second patent as against first patent flour was also shown previously (Berck, 1968b), and is presumed to be due mainly to the 20–25% greater ash (mineral) content, manifested by the greater amount of outer seed coat (bran layers) in second patent flour, and also the 5–8% greater protein content. Both the nature and amount of mineral and protein components are evidently factors in greater sorption affinity for PH_3, and may predominate over the inhibiting effect of low moisture content, as is shown by other substrates in Table I.

Sorption of PH_3 by middlings, shorts, bran, semolina, wheat germ, wheat gluten, and soy flour is modest to high, with sorp-

tion increasing with temperature—i.e., chemisorption. Conversely, wheat starch (item 13) shows a descending sorption pattern that indicates physical sorption. It should be noted that for both bran and wheat germ (items 10 and 12) a 6-inch column was used because of their large volume:weight ratios. On an equal weight basis, the sorption by bran would be greater than shown. The comparatively low uptake of PH_3 by wheat germ was shown previously (Berck, 1968b).

Differences in PH_3 uptake between a low-protein substrate such as wheat starch (item 13, 0.2% protein) and materials of high protein content such as gluten (85%), soy flour (52%) and fish protein concentrate (75%), and also mixed amino acids as in casein hydrolysate (94% protein) (items 14 to 17, Table I) are clearly shown. The length of column packed with fish protein concentrate (FPC) powder could not exceed 1 inch if temperature effects were to be evident. FPC powder has a notably high mineral content (17.1%), which could enhance its affinity for PH_3. The role of high protein and mineral content in this regard has been previously discussed (Berck, 1968b).

Aluminum oxide, Merck, (item 18, Table I) showed some physisorption characteristics but was a satisfactory trap for S-containing gases, such as SO_2, H_2S, COS, CH_3SH, and CS_2. These gases, if present in excessive amounts, interfere with determination of PH_3 by the FPD method (Berck et al., 1970). Based on equivalent weights in $1\frac{1}{2}$-inch columns, the Merck Al_2O_3 sorbed approximately 22% less PH_3 than the Woelm Al_2O_3.

Differences in sorptive power were also shown by the three soil types (items 19 to 21, Table I). The sorption of PH_3 by peat soil changed little with change of temperature from 50° to 110° C. In contrast, Yolo (montmorillonite) and particularly Ramona (mica) soils both showed strong chemisorption at the higher temperatures. Specific adsorption (chemisorption) of low concentrations of SO_2 by Fe_3O_4 and Al_2O_3 aerocolloidally dispersed was found by Smith et al. (1969). Many other examples of chemical (irreversible) binding of gases, including inert gases such as N_2, by inorganic systems can be found in the scientific literature (Deitz, 1956; Gregg and Sing, 1967; Hayward and Trapnell, 1964).

Table II shows the percentage of applied PH_3 sorbed by glass beads, four soil samples (three of which are also listed in Table I, but were retested 6 months later), and purified glutathione in oxidized and reduced forms. The column temperatures range from 45° to 120° C. in 25° increments. Glass beads (item 1) sorbed a small proportion of the applied PH_3 irrespective of temperature. In this regard, the slight alkaline nature of glass, both lime and borosilicate, as a possible factor in sorption of traces of acid gases should be noted. Differences between the peat and mica soils of Tables I and II are related to differences in weight of substrate, but differences between the Yolo samples cannot be so explained. Nevertheless, similar trends were obtained both in Tables I and II, respectively. A 5-year-old laboratory sample of Zaca soil (item 5) low in organic matter and high in minerals, showed marked chemisorption. The results with soils suggest that this technique may be of assistance in characterizing soil types by differences in sorption affinity. Reduced glutathione (GSHG, item 7) of which there was a greater weight, sorbed more PH_3 than did oxidized glutathione, GSSG (item 6). This difference would be slightly reversed if the respective sorption data were compared on a basis of equal weight rather than equal column length. However, we noted that an increase in weight of substrate—e.g., 50%—is not accompanied by a proportionate increase in sorption (see also Berck,

1968b). In general, when the concentration of PH_3 of a given injection was lowered, a larger fraction of the amount applied was sorbed. Packed columns of varied length were used in the current investigation mainly for convenience, because by varying the length of packed zone, changes in PH_3 uptake in response to temperature could be measured without excessive prolongation of retention time.

Table III shows the variability in sorption of PH_3 obtained in six small and six large 2-inch glass columns packed with first and second patent flours, feed middlings, shorts, gluten powder, and soy flour, respectively. The larger columns were used as a means of determining the effect on PH_3 sorption at column temperatures of $45°$, $70°$, and $95°$ C. of a four-to fivefold increase in amount of substrate, using column lengths essentially the same as their smaller counterparts. This was done by fusing 13-mm. glass tubing to 6.5-mm. tubing to yield columns of larger capacity. Tests were made 6 months after those of Table I. Only the gluten and soy flour of Table III were of the same source as in Table I.

On the basis of the mean % sorption (Groups A and B, Table III), both first and second patent flours showed little change in PH_3 uptake due to rising temperature. Second patent flour sorbed more PH_3 than did first patent flour, as was similarly shown in Table I. Standard deviations from the mean in Groups A and B ranged from 1.09 to 3.60 and the standard errors from 0.44 to 1.47. Although the large columns contained about five times as much substrate by weight as did the small columns, sorption increased only by factors of approximately 2.0 and 1.6 for first and second patent flours, respectively. In cross-reference to data obtained in this regard in previous experiments with a static system, doubling the weight of wheat of 15.0% moisture content at $35°$ C. increased the sorption by a factor of 1.28–1.31 (Berck, 1968b, Table II). If the inverse relationships between free PH_3 and amount of substrate shown in the latter experiments were extrapolated to a fivefold increase at $35°$ C., the increase factor would be only 1.45. The sorption increase factor is apparently related to the asymptotic form of isotherms for PH_3 (Berck and Gunther, unpublished data, 1969), and will in any event depend on the nature of the substrate, temperature, and period of exposure. It is thus not possible to extrapolate % sorption to weight of substrate on a linear basis.

Middlings and shorts (Groups C and D, Table III) showed intermediate chemisorption power, as was shown in Table I, and also in a previous investigation (Berck, 1968b). The range of standard deviation for middlings and shorts was 2.69–5.26 and 1.90–4.68, respectively, and the standard error range was 1.10–2.15 and 0.77–1.91, respectively. Increase in weight of substrate in the large columns by 4.5–5 times that of the small columns resulted in a 15–25% increase in PH_3 sorbed (factors of 1.15–1.25), depending on the column temperature.

Gluten and soy flour (Groups E and F, Table III) sorbed PH_3 strongly and per cent sorption increased with temperature (chemisorption). No PH_3 passed through the large-diameter columns packed with soy flour. Sorption of PH_3 by gluten powder increased by not more than 10% (factors of 1.03–1.10) when fivefold extra weight of substrate was packed in the larger columns. It is perhaps to be expected that the increase in sorption will become progressively smaller when the sorption affinity of substrates increases. This further emphasizes the need for caution in any extrapolation of results from laboratory investigations to the actual uptake of PH_3 by products under commercial conditions.

The data of Tables I, II, and III illustrate a wide range of sorption affinities for PH_3 by various substrates as compared with the FPD response obtained with an empty column, with 500 picograms PH_3 injected in triplicate in each case at the various test temperatures. We considered that for cross-reference purposes an empty column would better meet our requirements than a well-conditioned analytical column, since sorption by the inner walls of the empty column would more probably be matched, and thus automatically cancelled in intercomparison, by equal sorption by the walls of the packed short columns.

Among our preliminary tests, freshly packed, unconditioned 3-inch columns of Porapak Q, 80–100 mesh; Porapak S, 100–120 mesh; and 3% Carbowax 20M on Gas-Chrom Q, 60–80 mesh, all showed appreciable uptake (30–55%, depending on the column temperature) of a 500-picogram injection of PH_3. However, sorption was increasingly less (manifested by progressively higher peaks) as additional charges were injected. Such a trend was also noted between successive injections into columns packed with materials of low- to intermediate-sorption characteristics, such as first and second patent flours, wheat starch, wheat germ, and semolina. In this regard, it is a common experience in use of GLC and especially GSC columns that multiple injections of sample may be needed to saturate the reactive sites of a new column after conditioning before the column can be used for quantitative separation and measurement of desired components. Gas chromatography itself is a physical process consisting of a downstream migration of thousands of rapidly alternating cycles of sorption–desorption between the mobile and stationary phase, and becomes quantitatively useful within certain concentration limits after chemisorption (specific adsorption) sites are saturated. Chemisorption is considered to be confined to a single monolayer.

Nearly all the PH_3 peaks in this investigation were remarkably sharp and symmetrical (see Figure 2, Berck et al., 1970) with no diffuse front or tailing rear, such as often accompanies physical sorption, particularly when column temperatures or amounts of substrate are increased. The few exceptions to perfect peak symmetry were those measured at an attenuation of $8\times$ (e.g., soy, gluten, FPC, casein hydrolysate), where instrumental fluctuations produced a slight jog in the base line immediately at the termination of the peak base.

The net PH_3 residence time, measured by the difference in retention time, t_R, between that of a packed column assembly and an empty column of the same total length, varied from 0.5 to 6 seconds, depending on the nature, length, and temperature of the column packing. According to Kiselev et al., (1964), the t_R and band broadening in GC, apart from the flow rate of carrier gas and the length of column packing, are determined by the geometrical structure of the adsorbent, by the thermal motion of the molecules (column temperature and molecular weight), and by the rates of adsorption and desorption. The latter are governed by the temperature, geometry, and chemical nature of the adsorbent surface as well as by the electron density distribution and geometrical structure of the adsorbate molecules (Kieselev et al., 1964). Direct comparison between the peak heights yielded by injections of PH_3 in empty and packed column assemblies is somewhat in error because of resultant differences in t_R. While t_R is inversely related to the flow rate of the carrier gas, correction of t_R to directly comparable conditions is complicated because of the pressure drop across each packed column, and the considerable differences in porosity and particle size of substrate and other physical factors. It was not possible

under our conditions to change N_2 flow rates for each packed column to obtain a comparable base for t_R at each temperature without at the same time affecting other operational factors involved in the FPD response. However, use of short columns helped to restrict changes in t_R to a minimum.

Injection of 500 pg. of PH_3 per sample was predicated on the capability of the FPD method (Berck et al., 1970) to measure 5 ± 0.3 picograms of PH_3. The latter concentration corresponds to 5 ppt for a 1-gram sample. Since chemisorption involves only a small fraction of the total concentration of gas or vapor—e.g., corrosion of steel surfaces by atmospheric O_2 and water vapor—ability to discern differences of 1% in uptake is enhanced by using small rather than large amounts of adsorbate gas to reduce the swamping effect of physisorption. Such ability depends on the combined capabilities of the analytical method and experimental conditions.

Investigations of chemisorption are usually preceded by outgassing the substrate at high temperatures (200°–350° C.) for periods of $^1/_2$ to 8 hours either with or without vacuum. Such a procedure would exclude heat-sensitive materials such as were used in the present investigation, where temperatures higher than 100° C. would certainly reduce the moisture levels and thus change the characteristics of the substrate. Our use of short outgassing periods of 2 minutes with N_2 at each temperature is closer to actual commercial conditions, which are generally of a static nature and do not involve outgassing prior to fumigation. Furthermore, although temperatures in the 45°–100° C. range for cereal products are considerably higher than those encountered in commercial practice, they enable observation of changes in sorption that are keyed to the short contact periods (0.5–6 seconds) used herein.

The continuous flow method such as used herein was first used by Nelsen and Eggertsen (1958) to determine the surface area of cracking catalysts by measuring adsorption of N_2 at $-196°$ C. from a mixture of N_2 and helium, using GC with thermal conductivity detection. Roth and Ellwood (1959), also using thermal conductivity detection, improved the Nelsen-Eggertsen method for determination of surface area by calibrating their prepared mixtures along with each desorption, thus eliminating the need to measure absolute flow rates. Gruber (1962) utilized chemisorption of CO at room temperature to determine the specific metal surface

areas of multicomponent catalysts, which correspond to only 0.1 to 1% of the total surface area. The amount of CO chemisorbed was obtained by difference.

The investigation reported herein is, to the best of our knowledge, the first application of dynamic conditions to measure the sorption affinities of cereals and miscellaneous products toward fumigant gases.

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